



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re application of:

Helmut MANGOLD et al.

Application No. 10/020,920

Confirmation No. 8866

Filed: December 19, 2001

For: PYROGENIC OXIDES DOPED
WITH POTASSIUM

Art Unit: 1793

Examiner: N.Y. M. Nguyen

Atty. Docket No.: 39509- 176287

Customer No.

26694

PATENT TRADEMARK OFFICE

APPEAL BRIEF

Sir:

This is an appeal to the Board of Patent Appeals and Interferences from the final rejection set forth in the Office Action of August 16, 2007. Appellants timely filed a Notice of Appeal and a Request for an Extension of Time on January 29, 2008.

Appellant submits herewith an Appeal Brief, pursuant to 37 C.F.R. §41.37(c). The Commissioner is authorized to charge the required fee to Deposit Account No. 22-0261. However, should an additional fee be required other than the amounts previously paid to the U.S. P.T.O., the Commissioner is authorized to charge Deposit Account No. 22-0261 for the purposes of maintaining the pending status of this application.

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(1) REAL PARTY IN INTEREST

The Assignee of this Application, and thus the real party of interest in this Appeal, is Evonik Degussa GmbH, having a business address at Rodenbacher Chaussee 4, 63457 Hanau Germany.

(2) RELATED APPEAL AND INTERFERENCES

No appeal or interferences are known to Appellants or the Appellants' legal representative for Assignee which would directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) STATUS OF CLAIMS

The Application was filed with claims 1-5.

Claims 1-5 were amended and claims 6 and 7 added by a preliminary amendment.

Claim 1 was amended in the Amendment submitted on December 12, 2003.

A Rule 116 Amendment was submitted on June 16, 2004 and was not entered.

Claims 8-10 were added with a first Request for Continued Examination (RCE) submitted July 22, 2004.

Claim 4 was amended and claim 11 added in the Amendment submitted February 2, 2005.

Claims 1, 3 and 4 were amended and claim 8 cancelled in an Amendment submitted October 21, 2005.

Claims 1 and 4 were amended in an Amendment submitted June 14, 2006.

A Rule 116 Amendment amending claims 1, 4, 5 and 10 and cancelling claim 2 and 9 was submitted January 26, 2007 but not entered.

A second RCE was filed February 21, 2007 requesting entry of the Amendment submitted January 26, 2007.

Claims 1, 4 and 10 were amended in an Amendment submitted June 5, 2007.

Claims 1, 3-7 and 10-11 were finally rejected in the Office Action mailed August 16, 2007. These are the claims pending in the application, with claims 1, 4 and 10 being the independent claims. Claims 2 and 8-9 have been cancelled.

Claims 1, 3-7 and 10-11 are appealed and set forth in the Appendix to this Appeal Brief.

(4) STATUS OF AMENDMENTS

After the final Office Action dated January 20, 2006, Appellants filed the Notice of Appeal. No amendments were filed after the final Office Action that is being appealed.

(5) SUMMARY OF THE CLAIMED INVENTION

The claims are directed to a novel product (claims 1, 3 and 5) and a novel method for its preparation (Claims 4, 6, 7 and 10-11).¹ The product is directed to a narrow distribution of pyrogenically produced potassium-doped metal or metalloid oxide particles, having a breadth of distribution of particle size of at least 0.7. (See, for example, lines 14-15 on page two of the

¹ The instant specification discusses the unexpected nature of the morphological changes in potassium doped pyrogenically produced silica particles first seen at a minimum potassium concentration. The morphological change in particle concentration permits one to achieve the claimed narrow particle size distribution in a two step process without the need of filtration. Such a narrow distribution of particle sizes was not recognized for potassium doped pyrogenically produced silica prior to Appellants' work.

specification.) The particles are further characterized as having a BET surface between 1 and 1000 m²/g and a homogeneously distributed amount of dopant in the range from 500 to 20,000 ppm. The product is suitable for chemical mechanical polishing (CMP) applications. (See, for example, page 4 of the specification in the paragraph starting at line 17.) The claimed method of preparation requires two steps. The first is the feeding of an aerosol-gaseous mixture into a flame under conditions suitable for producing pyrogenic oxides by flame oxidation or flame hydrolysis to form the potassium-doped pyrogenic oxide spherical particle product having a distribution of particle size of at least 0.7. The second is the direct recovery of the identified pyrogenic-doped oxide particle product directly from the reacted aerosol-gaseous mixture. Critical to obtaining the distribution is the use of an aerosol with a concentration of a potassium salt of more than 0.5% by wt. (See, for example, page 3 of the specification at lines 4-18). The morphology changes and narrow distribution of particles are apparent from Figures 11A -13B (Table 4 and Example 7 (20% potassium dopant)). Figures 8A-10B (Table 3 and Example 1) illustrate the results obtained in the absence of a dopant.

(6) GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

The grounds of rejection for review are as follows:

A. Whether claims 1-7 and 9-11 are properly rejected under 35 U.S.C. § 103(a) as being unpatentable over CA 2,223,377 (Mangold et al.) taken in view of Vanell (US 6,423,638) or Hall et al. (US 6,372,648)?

(7) ARGUMENT

A. Whether claims 1-7 and 9-11 are properly rejected under 35 U.S.C. § 103(a) as being unpatentable over CA 2,223,377 (Mangold et al.) taken in view of Vanell (US 6,423,638) or Hall et al. (US 6,372,648)?

1. Argument for method claim 10

CA 2,223,377 does not teach or suggest a two step method where an aerosol formed from an aqueous solution having a potassium salt concentration of more than five percent by weight is used in a first step to produce potassium doped pyrogenically produced metal or metalloid oxide particle product having a breadth of distribution of particle sizes of at least 0.7 which product is directly recovered from the gaseous reaction mixture, formed in the first step, in the second step.

Claim 10 method is limited to the two recited steps since it employs "consisting of" as the word of transition.² The claimed aerosol has a potassium salt concentration greater than 0.5% by weight. The claimed product comprising pyrogenic-doped oxide particles having a breadth of particle distribution of at least 0.7 is recovered directly from the reacted aerosol aerosol-gaseous mixture.

In contrast to the claimed method, CA 2,223,337 (Mangold et al.) teach a process for preparing doped, pyrogenically produced metals and/or metalloid oxide particles using flame hydrolysis techniques. No range of potassium salts is expressly taught and no purpose, other than doping is taught for the dopant material. Various uses of the doped pyrogenically produced

² See MPEP 2111.03 and cases cited therein. The transition word "consisting of" excludes any element, step or ingredient not specified in the claim. *In re Gray*, 53 F.2d 520, 11 USPQ 255 (CCPA 1931).

metal and/or non-metal oxide are listed. Included in the list is CMP applications. Doping with cerium and potassium are exemplified. Example 5 is the only teaching dealing with potassium salt amounts, which amount is limited to 0.5% by weight.³ The recovered product is not characterized in terms of particle size distribution. The product is described as a white, finely divided powder.

The experimental conditions mentioned in Example 5 of CA 2,223,337 differ from those described in the instant specification, e.g. additional oxygen.⁴ The characteristics of the recovered product of the reference also differs from that recovered by Appellants.⁵ These differences in product characteristics and experimental conditions, together, suggest the process as claimed is distinct from CA 2,223,337.

It is clear that CA2,223,337 does not teach the process as claimed. The Examiner also recognizes this since the rejection based on anticipation by the "primary" reference was withdrawn.⁶

³ Please note that the claims exclude this amount and that the instant examples specify higher concentrations.

⁴ Table 1 of the reference and Table 1 of the instant specification (p. 20) set forth experimental conditions. Only the SiCl₄ are clearly the same. The others clearly differ in amounts, e.g. Primary or are not mentioned at all, e.g. additional oxygen.

⁵ Table 2 of the reference and Table 2 in the specification (p.21) describe the characteristics of the recovered product. Some characteristics are mentioned in both tables. Some characteristics, e.g. bulk density, DBP, stamping density are mentioned only in the instant specification.. The common characteristics clearly differ, e.g. BET, 199 v. 104, pH, 4.83 v 7.96. These product characteristic differences further suggest the differences in experimental conditions result in product differences.

⁶ The anticipation rejection based on the Canadian patent was withdrawn in the Office Action dated March 18, 2004. See page 3.

The applied references do not disclose, individually or collectively, a result-effective variable which has been deemed obvious to optimize and would arrive at the claimed potassium salt concentrations and the recovered product.⁷

CA 2,223,337 does not identify a correlation of the breadth of doped particle distribution with dopant concentration, in particular potassium salt concentration. There is no mention of a range of potassium salt concentrations. There is a range of concentrations for dopants. There is no teaching within CA 2,223,337 that correlates dopant concentrations, especially potassium salts, with obtaining a narrow range of particle size distribution.⁸ It is not seen how it would have been obvious to arrive at the process as described by claim 10 by routine trial and error experimentation without a disclosure of potassium salt concentration as a result-effective variable. Further, the claim requires both that the amount of potassium salt be greater than 0.5% by weight and also that the resultant product having the claimed particle size distribution be directly recovered from the gaseous reaction mixture. There is no size based screening methodology. A cyclone or simple filter is used.

The secondary references, discussed below, are not directed to the manufacture of potassium doped pyrogenically produced metal or metalloid oxide particles. There is no mention of potassium salts in the context of being a result-effective variable relative to any property that would have led to the claimed potassium salt concentration.

⁷ A particular parameter must first be recognized as a result-effective variable before a determination of the optimum or workable ranges of said variable might be characterized as routine experimentation. *In re Antonie*, 559 F2d. 618, 195 USPQ 6 (CCPA 1977).

⁸ No rationale has been provided as to how optimization of the dopant concentration would lead to the claimed potassium salt concentrations and the recovery of doped metal or metalloid oxide particles having the narrow claimed breadth of distribution of particle size distribution of at least 0.7 particle. The method of Claim 10 clearly does this in only two steps. There is no ornate filtration/screening process.

The claim requires the recovery of a specified product; knowledge of the existence of that product would have been required so that it would have been obvious to recover. There is no disclosure of the product other than in the instant specification.

The CA 2,223, 337 in Example 5 teaches the recovery of its product by a filter or cyclone. This mode of recovery is disclosed by Appellants in the specification. The experimental conditions, however, would have to be the same or similar to those employed by Appellants for the claimed product to be inherently recovered. This does not appear to be the case. The Appellants' experimental conditions are distinct from those taught in Example 5 of CA 2,223, 337. See footnote 4. It would be speculative to assume that the claimed product would be inherently recovered since the experimental conditions are different and result in different product characteristics. See footnote 5. The Examiner no longer relies on anticipation so apparently he agrees that the conditions are different. See footnote 6. Any reliance on Appellants' disclosure would involve the use of impermissible hindsight.

The secondary references fail to remedy the deficiencies of the primary reference since they contain no teaching of potassium salts as a result-effective variable, which if optimized, would lead to the claimed potassium salt concentration.

Vanell (US 6,423,638) does not provide a teaching of a result-effective variable, which if optimized would result in the claimed concentration and the claimed process described by claim 10. The Vanell teaching is not directed to the manufacture of doped particles but rather is concerned with a storage problem associated with "down stream" use of dispersions of colloidal silica. Vanell teaches a "non-plugging" filter design for removing agglomerated or aggregated colloidal silica particles from a dispersion. The filtered dispersion of colloidal silica is used for

planarizing semiconductor wafers at site of operation.⁹ The presence of larger particles in the colloidal silica dispersions lead to the "scratching" of wafers in CMP applications. The use of Vanell filters at the CMP site removes the larger particles prior to use.

Vanell does indicate that ideally a polishing slurry would comprise abrasive particles having a size distribution in a narrow range. There is no mention of how one can achieve this starting with a gaseous reaction mixture like that taught in the CA 2,223,337 manufacturing process. Mere mention of the desirability of monodispersions (a breadth of distribution of particle size of 1) in the context of CMP applications does not provide the necessary guidance which would have allowed one to obtain a product like that claimed directly from a gaseous reaction mixtures in two steps like that claimed.

Hall et al. (US 6,372,648) does not provide a teaching of a result-effective variable, which if optimized, would result in the claimed concentration and the recovery of the claimed product. Hall et al. is not directed to a manufacturing process involving doped pyrogenic particles. Rather, Hall et al. teach a chemical mechanical polishing slurry with functionalized silica abrasive particles.¹⁰ The functionalization permits use of the silanized silica particles at high pH values where silica particles normally degrade.

⁹ Vanell is concerned with the development of a filter capable of use with a colloidal suspension in real-time. Vanell achieves this, in part, by breaking apart agglomerates prior to filtering. See col. 4, lines 43-52. The materials mentioned by Vanell as applicable for their approach are silicon dioxide particles formed either by chemical vapor deposition of SiCl₄ or by colloidal methods. These particles form aggregates having sizes of at least 150 nanometers. See col. 15, lines 45-59. Vanell clearly states that 1) the well known processes of filtering are inadequate for filtering colloidal suspensions because of high particle counts in suspension, 2) filters rapidly blind and plug up and 3) removing too many of the particles can also change the chemistry of the colloidal suspension making it unstable for the application. See col. 19, lines 38-44.

¹⁰ Hall et al is concerned with functionalized oxides (chemically treated oxides) in the context of abrasives to be used in CMP. The functionalization imparts stability to the particles in alkaline environments by preventing degradation

There is no mention in Hall et al. of potassium or potassium salt concentrations as a factor in controlling the breadth of particle size distributions in such manufacturing processes. Mere mention of the desirability of monodispersions in the context of CMP applications does not provide the necessary guidance which would have allowed one to obtain a product like that claimed directly from a gaseous reaction mixtures in a two step process like that claimed.

The secondary references do not suggest their combinability with the primary reference.¹¹

While the primary and secondary references mention CMP applications, there is no apparent problem existing in the primary reference for which the Vanell filter or the Hall et al silanization process would be sought as a solution. The silica types in Vanell are not pyrogenically produced nor are they potassium doped pyrogenically produced silica particles. CA 2,223,377 does not mention the presence of large particles produced by agglomeration or aggregation or conditions which would result in their production. The Vanell filter is directed to the filtration of stored aqueous dispersions which required filtration prior to use on site in a CMP process on site. Further, the inclusion of such a filtration step would be precluded by "consisting of." Examiner has not provided a satisfactory explanation or citation as to why the closed nature of "consisting of" can be ignored. Claim 10 is limited to two steps and recovers a desired product suitable for CMP use.

Hall et al. is directed to silanization of silica to impart stability at alkaline pH. The Examiner has not provided a satisfactory explanation or a citation as to why one would ignore the

¹¹ When prior art references require selective combination by the court to render obvious a subsequent invention, there must be some reason for the combination other than the hindsight gleaned from the invention itself...Something in the prior art as a whole must suggest the desirability, and thus the obviousness of making the combination." Uniroyal, Inc. v. Rudkin-Wiley, Corp., 837 F. 2d 1044, 1051, 5 USPQ2d 1434, 1438 (Fed. Cir. 1988).

closed nature "consisting of " as a word of transition. Claim 10, as written, would preclude a silanization step.

The Vanell reference directed to dispersions containing precipitated silica does not provide sufficient guidance as to how to adapt its teaching to potassium doped pyrogenically produced silica recovered from a gaseous phase.

Examiner suggests any particle size range present in the Example 5 product of CA 2,223,337, whether narrow or wide, needs attention and can be further narrowed by filtration. Note Vanell teaches that there are downsides to filtration. See background section and col. 19 lines 32-49. Only colloidal products are exemplified by Vanell. No specific detailed guidance exists as to pyrogenic silica. There is unpredictability as to actual benefits to be obtained.¹² A dispersion of pyrogenic silica would be expected to gel over time unless properly treated. A highly viscous liquid would not be amenable to filtration where ease of flow is required. There is no teaching cited by the Examiner as to how address the viscosity issue.

2. Argument for method claims 4, 6-7 and 11¹³

The process described in claim 4 is similar to claim 10 except that claim 10 employs "comprising" as a word of transition and therefore is open to the presence of additional steps.

Claim 4, like claim 10, requires the presence of a potassium salt concentration more than 0. 5% by wt. and requires the recovery of potassium doped pyrogenically produced silica

¹² Dispersions of pyrogenic silica unless properly prepared will gel and lose fluidity. See Reference Example 1 of U.S. Patent 5,967,964. See Zhenwu Lin, Joseph Zahka and Geanne Vasilopoulos "POU Filtration of Silica-Based CMP Slurries Using Planatgard TM Filters", Mykrolis Applications Note MA071 where filter plugging is discussed.

¹³ Claims 6-7 and 11 depend on claim 4. These claims are not separately argued.

particles having the claimed narrow range of particle sizes and also having the specified concentration of potassium distributed equally within the particles.¹⁴

The arguments presented above relative to potassium salt concentration and the recovery of potassium doped pyrogenically produced metal or metalloid oxide particles having a breadth of distribution of particle size of at least 0.7 are equally applicable here. The closed nature or open nature of the transition would not impact the arguments.

3. Argument for product claims 1-3

Claim 1, a product by process claim, is directed to potassium doped pyrogenically produced metal or metalloid, e.g. silica, particles having 0.03 to 20% by weight potassium uniformly distributed within the particles and with a "narrow" distribution of particle sizes, breadth of the distribution of particle size of at least 0.7. (One represents a monodispersion.) Claim 3 further limits the product defined in claim 5 by the DBP values which correspond to minimum structure (Figure 4).

The primary reference does not reasonably teach the product or render it obvious.

It is not seen that CA 2,223,377 fairly teaches, suggests or renders obvious the product claimed. There is no mention in CA 2,223,377 of a particle size distribution like that claimed. There are differences in the preparatory methods, e.g. concentration of the potassium salt. See footnote 4. There are also clear differences in the measured and comparable product characteristics. See footnote 5.

¹⁴ The instant specification discusses the unexpected nature of the morphological changes in potassium doped pyrogenically produced silica particle first seen at a minimum potassium concentration. The morphological change in particle concentration permits one to achieve the claimed narrow particle size distribution in a two step process without the need of filtration. Such a narrow distribution of particle sizes was not recognized for potassium doped pyrogenically

The secondary references provide no guidance as to how the CA product could be modified to arrive at the product claimed.

The teachings of Vanell and Hall et al are discussed above. Both references teach the desirability of “monodispersions” in CMP processes. Neither secondary reference teaches how to get there starting with potassium doped pyrogenically produced metal or metalloid oxide particles. Further, neither secondary reference provides a teaching which would suggest that the claimed product is inherently recovered in Example 5 of the Canadian Patent. Appellants produce the claimed product from a gaseous reaction mixture in two steps.

The Examiner's Position

According to the final Office Action dated August 16, 2007, the Examiner asserts the subject matter as a whole is obvious since it would have been obvious to select the portion of the prior art's range which is within the Applicants' range because it has been held prima facie obvious to select a value in a known range by optimization for results.¹⁵ Appellants disagree for the reasons stated above including: A potassium salt range is not taught by the references. There is no teaching of a result dependent variable that depends on potassium salt concentration. There is no teaching in the references that a dopant concentration affects the range of particle size

produced silica prior to Applicants' work.

¹⁵ *In re Boesch*, 617 F.2d 272, 205 USPQ 215 (Fed. Cir. 1988). There is no range of potassium salts expressly taught in the reference. There is no function for potassium salt concentration taught in the reference, which if optimized would have resulted in the claimed concentration. The case does not suggest that one can optimize in a vacuum. One must know that there is a correlation between a variable and a property one wishes to optimize. Here, there is not even a stated reason to select potassium salt concentration or the potassium concentration for optimization amongst other possible parameters.

distribution.

Further, the Examiner asserts that the subject matter as a whole would have been obvious to one of ordinary skill in the art at the time the invention was made because overlapping ranges have been held to be prima facie obvious.¹⁶ Appellant disagrees for the reasons set forth above which include: The Examiner admits that CA 2,223,377 does not disclose specifically the distribution of particle size, the pH or the absorption of dibutylphthalate of the oxide product (claim 3). The Examiner urges that if the CA 2,223,377 product does not inherently possess these characteristics (the anticipation rejection was dropped), it would be obvious to subject the product to a screening process to obtain a monodispersed product since the desire to obtain a monodispersed product is well known in the art (Vanell (column 2 at lines 47-50)), Hall et al. (paragraph bridging columns 1-2)). Appellant again disagrees for the reasons argued above including there is no teaching in any of the references as to how this can be achieved for potassium doped silica.

The Examiner agrees that claim 10 includes "consisting of " as a transition phrase but asserts that its significance can be ignored since there is insufficient evidence to show that the narrow particle size cannot be obtained through mere trial and error experimentation.

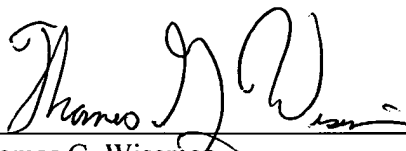
¹⁶ *In re Malagari*, 499 F.2d 1297, 182 USPQ 549 (CCPA 1974). There is no overlapping range of potassium salt concentrations. The case does not suggest that one can optimize in a vacuum. One must know that there is a correlation between a variable and a property one wishes to optimize. Here, there is no stated reason to select potassium salt concentration or the potassium concentration for optimization amongst other possible variables.

The Examiner asserts that it would have been obvious to employ the Vanell filtration method to optimize the particle distribution range of CA 2,223,337 product, e.g. narrow the particle size distribution.

(8) CONCLUSION

For the foregoing reasons, it is respectfully submitted that claims 1-7 and 9-11 are patentable over CA 2,223,377 taken in view of Vanell (6,423,638) or Hall et al. (US 6,372,648). Accordingly, the Examiner's rejection of these claims should be reversed.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Thomas G. Wiseman", is written over a horizontal line.

Date: June 27, 2008

Thomas G. Wiseman
Registration No. 35,046
Venable LLP
P.O. Box 34385
Washington, D.C. 20004-9998
Telephone: (202) 344-4000
Telefax: (202) 344-8300

(9) CLAIM APPENDIX

Listing Of Claims:

Claim 1 (Previously presented): Spherically shaped potassium doped pyrogenically produced metal or metalloid oxide particles having a breadth of distribution of particle size of at least 0.7 and having uniformly distributed potassium from about 0.03% to 20% by weight and which are doped by means of aerosol with a potassium salt solution, characterized in that the spherically shaped pyrogenically produced particle base component is produced by flame oxidation or flame hydrolysis and wherein the doped oxide particles have a BET surface between 1 and 1000 m²/g, and wherein the pH of a 4 % aqueous dispersion of the doped particles is more than 5.

Claim 2 (Cancelled)

Claim 3 (Previously presented): The pyrogenically produced oxides of metals or metalloids in accordance with claim 1, further characterized in the absorption of dibutylphthalate does not allow any end point to be recognized.

Claim 4 (Previously presented): A method of producing potassium-doped pyrogenic oxide spherical particles having a uniformly distributed potassium content of more than about 0.03% by weight and having a breadth of the distribution of particle size of at least 0.7 comprising,

A) sequentially feeding a gaseous mixture, including a pyrogenic oxide precursor, and an aerosol to form an aerosol-gaseous mixture, which is fed into a flame under conditions suitable for producing pyrogenic oxides by flame oxidation or flame hydrolysis from the precursor, to form the

potassium-doped pyrogenic oxide spherical particles having a uniformly distributed potassium content of more than 0.03% by weight, and

B) recovering the formed pyrogenic-doped oxide spherical particles, which have BET surface of the doped oxide is between 1 and 1000 m²/g and the breadth of distribution of particle size of at least 0.7, from the reacted aerosol-gaseous mixture,

wherein the aerosol is homogeneously mixed before the reaction with the gaseous mixture and is prepared from a potassium chloride salt solution having a concentration of more than 0.5% by wt.

Claim 5 (Previously presented): A composition comprising the doped pyrogenic oxides of claim 1.

Claim 6 (Previously presented): The method of claim 4 wherein the aerosol is produced by atomization by means of an aerosol generator.

Claim 7 (Previously presented): The method of claim 6 wherein the atomization involves a gas-atomizing (two-fluid) nozzle method.

Claims 8 and 9 (Canceled)

Claim 10 (Previously presented): A method of producing potassium-doped pyrogenic oxide spherical particles with a breadth of the distribution of particle size of at least 0.7 and a uniformly distributed potassium content of more than about 0.03% by weight consisting of,

A) sequentially feeding a gaseous mixture, including a pyrogenic oxide precursor, and an aerosol to form an aerosol-gaseous mixture, which is fed into a flame under conditions suitable for

producing pyrogenic oxides by flame oxidation or flame hydrolysis from the precursor, to form the potassium-doped pyrogenic oxide spherical particles having a uniformly distributed potassium content of more than 0.03% by weight, and

B) recovering the formed pyrogenic-doped oxide spherical particles, which have BET surface of the doped oxide particles is between 1 and 1000 m²/g and have a breadth of the distribution of particle size of at least 0.7, from the reacted aerosol-gaseous mixture,

wherein the aerosol is homogeneously mixed before the reaction with the gaseous mixture and is prepared from a potassium salt solution having a concentration of more than 0.5% by wt.

Claim 11 (Previously presented): The method of claim 4 further comprising adding oxygen prior to the separation step.

(10) EVIDENCE APPENDIX

U.S. Patent 5,967,964 (Tab A)

Zhenwu Lin, Joseph Zahka and Geanne Vasilopoulos "POU Filtration of Silica-Based
CMP Slurries Using Planatgard[™] Filters", Mykrolis Applications Note MA071 (Tab B)

(11) RELATED PROCEEDINGS APPENDIX

None

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POU Filtration of Silica-Based CMP Slurries Using Planargard™ Filters

Zhenwu Lin, Joseph Zahka and Geanne Vasilopoulos

Introduction

Chemical Mechanical Polishing (CMP) has become an enabling technology in semiconductor device manufacturing. The CMP process uses submicron (30 - 200 nm) silica slurries at a typical concentration of 10-13% solids. Typical silica slurries are known to contain a small number (10^4 to 10^6 counts/ml) of > 1.0 micron particles, which could potentially cause defects (microscratches) on the planarized wafer surfaces. The slurry solution presents unique challenges in delivery, filtration, and particle measurement.

The silica slurries used in the CMP process are stabilized suspensions of fine particles, typically 30 to 200 nm in size with concentrations ranging from 10 to 30%, in aqueous solutions with a specific pH. These slurries, which may need on-site dilution in the FABs, are applied directly onto the rotating pad to polish wafers and achieve global planarity. Fumed silica-based and "colloidal" silica-based slurries are the two families that are commercially available.

Fumed silica slurry is manufactured in two steps: 1) production of fumed silica (three-dimensional branched chain aggregates) by the vapor phase hydrolysis of silicon tetrachloride in a hydrogen oxygen flame [2]; 2) dispersion of fumed silica in aqueous medium with certain additives. Commercial fumed silica CMP slurries normally contain silica aggregates with mean particle sizes ranging from 100 nm to 200 nm. Figure 1a shows a SEM picture of typical silica aggregates.

"Colloidal" silica is produced from a dilute aqueous solution of water glass through deionization/nucleation, polymerization, particle growth and concentration steps [3]. All process steps are in the liquid phase. The silica particles formed are normally spherical. Commercial colloidal silica CMP slurries have particles with mean sizes ranging from 30 nm to 50 nm. Figure 1b shows a SEM picture of typical colloidal silica particles.

Filtration Needs

The typical specification for commercial silica slurries includes percent solids, pH, specific gravity, mean particle size and general (bulk) particle size distribution.

"POU Filtration of Silica-Based CMP Slurries Using Planargard™ Filters"

However, a small number of "large" particles ($>1\mu\text{m}$) have been found which fall outside of the specified size distribution. These particles, which can be aggregates, agglomerates. SEM images shown in Figures 2A and 2B confirm their existence. These large particles may come from agglomeration or local drying of slurry on shipping containers and in the distribution system. Gels may form due to pH shocks during dilution or temperature fluctuations during shipment and storage.

There is no definitive information available on what size or type of particles can cause microscratches and particle contamination on wafer surfaces. However, higher numbers of "large particles" have been found to cause higher incidence of microscratches and particle contamination on polished wafers. Slurry filtration has proven to be beneficial in reducing wafer defects and increasing yields in CMP processes[1].

A control oxide CMP polishing experiment was conducted using a commercial fumed silica slurry contaminated with 5 μm silica particles ($\sim 10^4$ particles/ml). The polishing were performed on an IPEC/Westech 472 tool using a standard oxide CMP recipe. The bare wafers were deposited with 1000 nm PECVD SiO_2 before polishing. Figure 3 and 4 show the surface scan results on the wafers polished with and without point-of-use filtration. A ten-fold reduction of light point defects was achieved by using a Planargard CMP5 filter at the POU.

Slurry Characterization

The main challenge of slurry filtration is to selectively retain the small number of defect-causing "large" particles (i.e., 10^4 to 10^6 counts/ml greater than $1\mu\text{m}$) without retaining the desirable, small particles (30 to 200 nm) present in very high concentration ($> 10^{15}$ counts/ml). There should be no measurable changes to the slurry's percent solids concentration and bulk particle size distribution before and after filtration. Therefore, filters to be used in CMP slurry filtration should be evaluated *in slurry* to validate their performance for the following attributes:

- Retention efficiency for "large" particles
- % solids content and bulk particle size distribution before and after filtration
- Throughput (Lifetime)

1. Detection of "Large" Particles

Quantitative determination of "large particles" is required to determine filter retention and a correlation between large particle concentration and wafer defects. There is no commercial particle counters available that can be used to detect the large particles (10^4 to 10^6 counts/ml $>1\mu\text{m}$) in the presence of bulk slurry particles ($> 10^{15}$ counts/ml), without substantial sample dilution. Various particle counters were evaluated to determine their ability to detect the large particles with maximum tolerance to high concentrations of small particles (minimum sample dilution) and with ease of

"POU Filtration of Silica-Based CMP Slurries Using Planargard™ Filters"

operation. We selected a light scattering instrument was selected for the slurry application.

A typical schematic of the particle counting system, shown in Figure 5, includes continuous on-line dilution of slurry. The dilution factor should be high enough to minimize the interference caused by small particles in the slurry. Figure 6 shows a typical profile of large particle concentrations in oxide slurry before and after filtration. Filter retention for particles of a specific size can then be calculated based on the particle concentration before and after filtration.

2. Measurement of Bulk Particle Size Distribution and Percent Solids

Bulk particle size distribution (PSD) can be measured by many techniques [4]. The two most commonly used techniques in CMP slurries are light scattering and chromatography (i.e., capillary hydrodynamic fractionation, (CHDF). The light scattering instrument used for slurry PSD measurement is based on photon correlation spectroscopy (PCS), also referred to as quasi-elastic light scattering (QELS) or time-dependent light-scattering. With PCS, the size information is obtained from the time dependent fluctuation of scattered intensity due to concentration fluctuations resulting from Brownian motion of particles[4].

CHDF is based on the size exclusion effects that occur when a dispersion of particles flows through a capillary tube. Laminar flow in the capillary tube has a parabolic velocity profile. Smaller particles can reach the slower streamline close to the tube wall due to Brownian motion, while larger particles cannot. Therefore, large particles exit the capillary tube faster than smaller ones. CHDF can be used to measure particles between 15 nm and 1 micron with up to 1% solids [5]. This method was used for slurry particle size distribution measurement.

Another PSD instrument is based on acoustic attenuation spectroscopy. When acoustic waves propagate through a medium with suspended particles, the acoustic beam will be further attenuated by the particles by a variety of mechanisms. The acoustic attenuation spectrum can be detected and then inverted to obtain a mean particle size, a particle size distribution, and a dispersion concentration.

The percent solids in slurry can be calculated by drying a slurry sample of known weight.

Performance of Planargard Filters

Filter performance should be evaluated in slurry to determine: (a) retention efficiency for large particles; (b) percent solids content and bulk particle size distribution before and after filtration; (c) filtration throughput. This information is necessary for CMP process engineers to implement proper filtration.

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Conventional microporous membrane filters will not work due to the high solids concentration in the slurry that forms a cake and plugs membrane quickly. Graded-density non-woven depth filters are preferred for this application. Filtration experiments were conducted with all-polypropylene graded-density Planargard™ filters using silica slurry in a single-pass configuration to simulate point-of-use applications. Feed and filtrate samples were taken and analyzed for large particle concentration, percent solids, and bulk particle size distribution. The filter retention efficiency is defined as:

$$\text{Retention} = \frac{\text{Concentration in feed} - \text{Concentration in filtrate}}{\text{Concentration in feed}} \times 100\%$$

The retention efficiency curves for various Planargard filters are shown in Figure 7.

Throughput was measured based on the differential pressure across the filter as a function of filtered volume. A typical plugging curve is illustrated in Figure 8, which shows a gradual increase in differential pressure across the filter. The differential pressure increases slowly initially, but then climbs rapidly as the filter reaches the end of life. Data analysis proves that the plugging process follows the complete plugging mechanism, which can be represented by a linear relationship between the inverse differential pressure across the filter (or $\Delta P_{\text{min}}/\Delta P$ in dimensionless form) and filtration volume. In this mechanism, the pressure drop across the filter increases slowly at the beginning, which will then increase exponentially. The importance of understanding the plugging process is to determine the filter change out time before the pressure drop reaches the region of exponential increase.

To maintain process control the filter should not affect the slurry's composition and the filter should have consistent retention throughout its useful lifetime. Figure 9 shows that filter retention remains fairly constant throughout its lifetime. Table I shows that the filter does not change the percent solids and mean particle size in the slurry, which is extremely important for a CMP process. As long as the solids concentration is not changed before and after filtration, the filter will not alter the bulk particle size distribution. Figure 10 shows the slurry's bulk particle size distribution in the feed and filtrates at 60% and 95% of the CMP5 filter's throughput.

Implementation Strategy

Implementation of silica slurry filtration depends on CMP process requirements, space availability, and the characteristics of the slurries. A number of field tests have demonstrated that point-of-use (POU) filtration at the tool can provide the most benefit

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in wafer defect reduction. Table II lists the normalized test results for oxide CMP with POU filtration.

Other filtration locations are at post-dilution, in the distribution loop, and at the slurry supply drum/tote.

It is strongly recommended that the implementation should start at POU filtration with higher retention filters to realize the maximum defect reduction benefits during CMP process development and qualification. To optimize the process, filtration at other locations can be used to supplement POU filter(s) and potentially to extend the life of POU filters.

Conclusion

"Large particles" have been detected in CMP slurries using an optical particle counter. SEM evaluation of slurry particles on membrane filters confirmed their existence. These defect-causing large particles may come from agglomeration, local drying of slurry on shipping containers and in the distribution system, and gel formation due to pH shocks during dilution and temperature fluctuations.

Graded-density depth filter can be used effectively to remove the defect-causing large particles without measurable change to slurry composition. Field test data have demonstrated the benefits of filtration on wafer defect reduction during CMP processes.

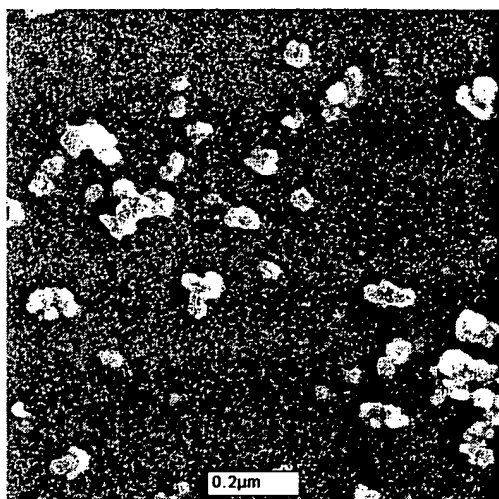
The optimal strategy to implement filtration in CMP processes can be dependent on site, process, and slurry type. POU filtration with higher retention filters is recommended to realize maximum defect reduction benefits during CMP process development and qualification.

References

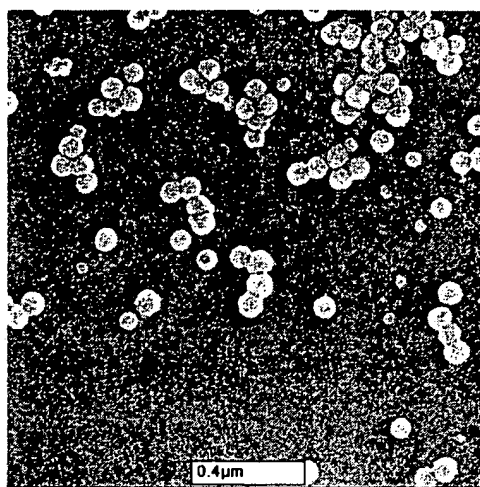
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Figure 1
Fumed Silica Aggregates and Colloidal Silica Particles



a. Fumed Silica SEM



b. Colloidal Silica SEM

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Figure 2
“Large Particles” and Gel in Silica Slurries

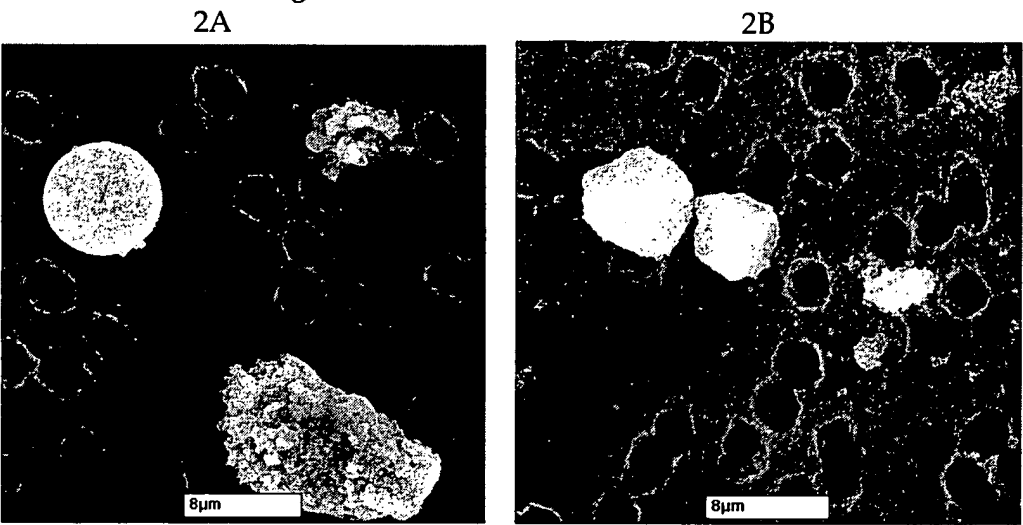
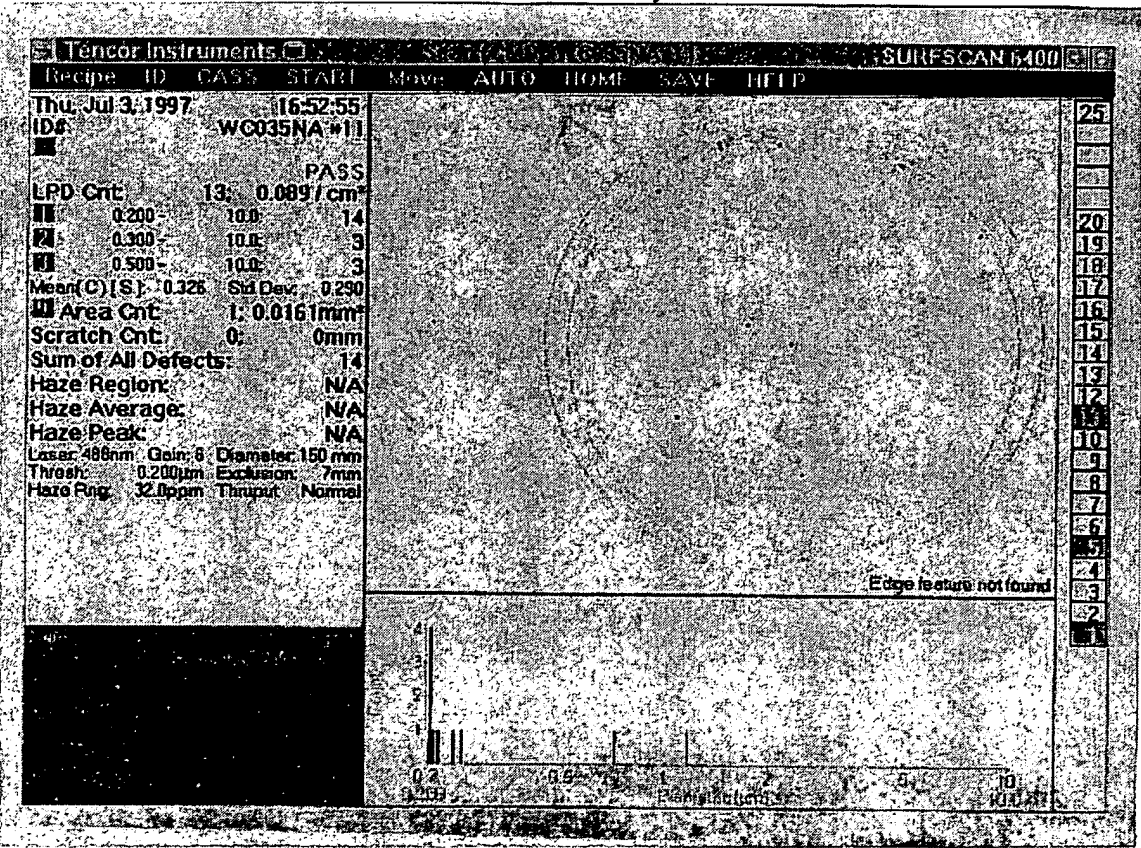


Figure 3 Wafer Scan Result Using Tencor SURFSCAN 6400 for the Wafer Polished with Filtered Slurry



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Figure 4 Wafer Scan Result Using Tencor SURFSCAN 6400 for the Wafer Polished with UN-filtered Slurry

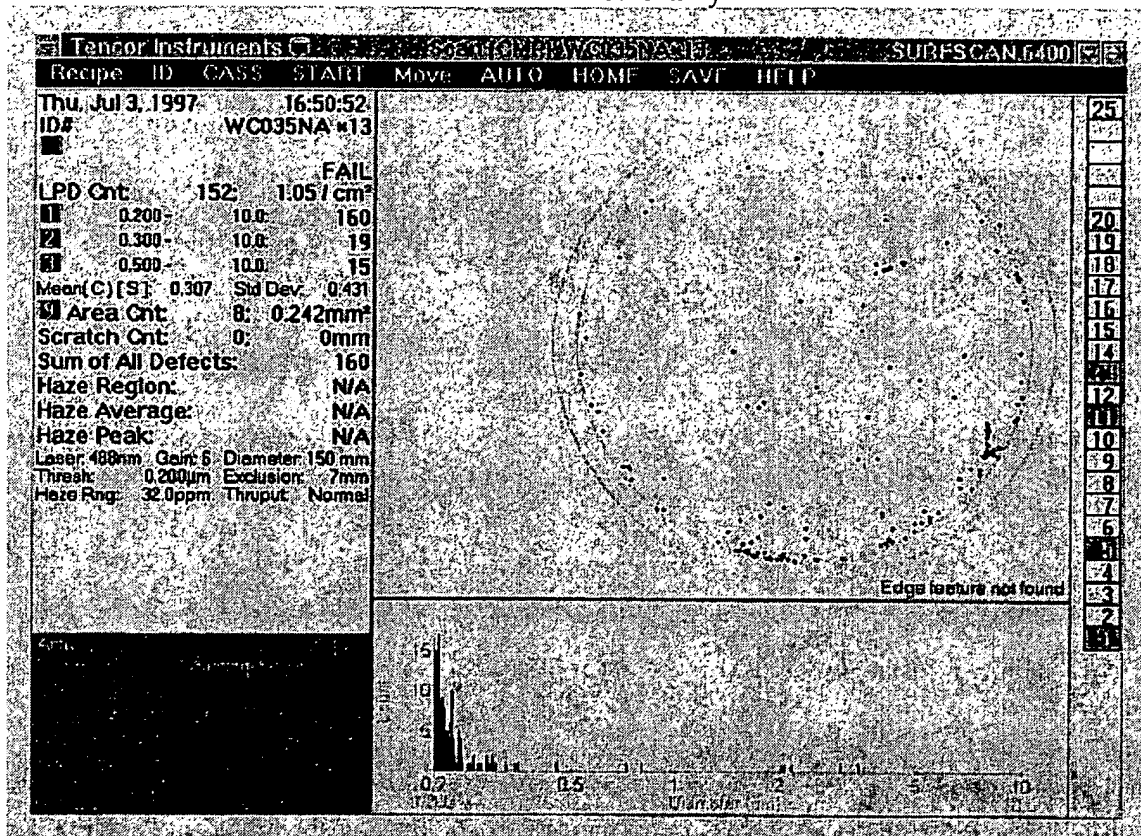
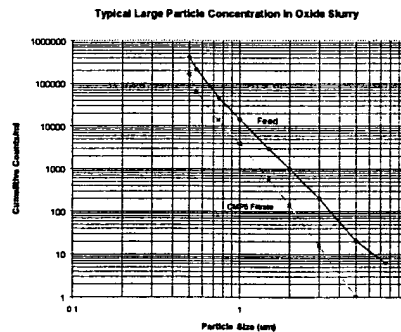
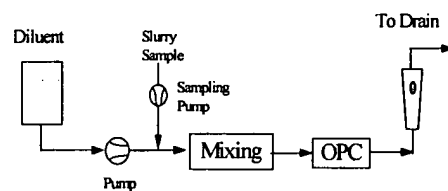


Figure 5

Figure 6

Schematic of Large Particle Counting System



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Figure 7
Retention Efficiency of POU
Planargard™ Filters

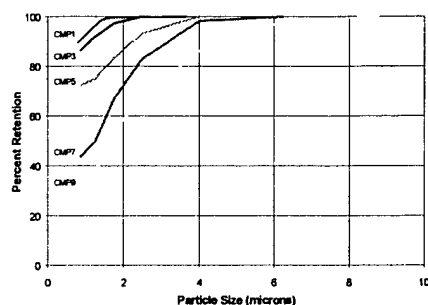


Figure 8
CMP5 Filter Plugging Curve
in Typical Silica Slurry

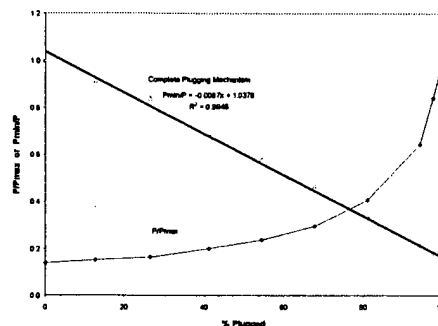


Figure 9
Retention Efficiency and Filter Life

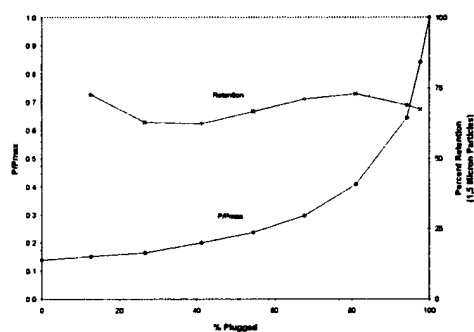


Figure 10
Effect of CMP5 Filter on
Slurry Bulk Particle Size Distribution.

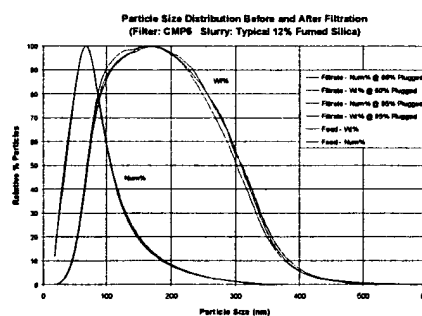


Table I
Effect of Filter Plugging on
Percent Solids and Mean Particle Size in Slurry

	Feed	60% Plugged	95% Plugged
% Solids	12.6	12.4	12.5
DW (nm)	192.3	197.	197.1
DN (nm)	93.3	93.3	94.1

DW: Mean diameter by weight
DN: Mean diameter by number

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Table II Field Test Results
Light Point Defect (LDP) Reduction by POU Slurry Filtration

Customer	Slurry	Filters Tested at POU	Normalized LPD Levels
A	Fumed Silica	None	100
		CMP5+CMP3	10
B	Colloidal Silica	None	100
		CMP7+CMP5	30
		CMP3+CMP1	9
C	Colloidal Silica	None	100
		CMP3	33

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